SECOND VIRIAL COEFFICIENT OF NON-POLAR GASES AND GAS MIXTURES AND BUCKINGHAM-CARRA-KONOWALOW POTENTIAL

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(*Received August* 8, 1966)

ABSTRACT. Second virial coefficient data of five rare gases, hydrogen and methane as a function of temperature have been interpreted on the three parameter intermolecular potential recently introduced by Carra' and Konowalow. Potential parameters have been determined for these seven pure gases. Combination rules have been derived which enable the determination of the unlike interactions from the knowledge of the related like interactions only. The second virial data of eight different binary gas pairs are also discussed. From these detailed investigations it has been concluded that this potential is somewhat superior to the two other widely studied three parameter potentials viz., the modified Buckingham exp-6 and Morse.

INTRODUCTION

A large number of intermolecular potentials have been used for computing the second virial coefficient, $B(T)$, of non-polar gases and gas mixtures. In this article we study in detail a three parameter potential recently introduced by Carra' and Konowalow (1964). This potential employs an exponential function to represent the repulsive overlap part of the intermolecular potential first suggested by Buckingham (1947) and is therefore more fully referred as Buckingham-Carra'-Konowalow potential. Hereafter this potential will be abbreviated as BCK. According to this the interaction potential energy, $\phi(r)$ is given by

$$\phi(r) = \epsilon \left(\frac{6+b}{b}\right) \left(\frac{r_m}{r}\right)^6 \left[\frac{6}{6+b} \exp\left\{b\left(1-\frac{r}{r_m}\right)\right\} - 1\right] \qquad \ldots (1)$$

Here r is the molecular separation distance, ϵ the depth of the potential energy minimum, r_m is the value of r for which $\phi(r)$ is a minimum, and b is a parameter which controls the slope of the repulsive limb.

Carrá and Konowalow (1964) determined the parameters of the BCK potential for neon, argon, krypton and xenon by using the crystal energy data and one value of the second virial coefficient. We determine the potential parameters for the five rare gases, hydrogen and methane employing only the $B(T)$ data as a function of temperzture. Making use of the expressions for the combination rules, also developed here, the B(T) data of eight different gas pairs as a function of tempera-

ture have been interpreted. Lastly, we present a comparative assessment of this potential in relation to the two other intermolecular potentials and show the supremacy of the BCK potential. The other two potentials are the familiar modified Buckingham exp-6 potential first used by Rice and Hirschfelder (1954) and the Morse potential exploited by Konowalow, Taylor and Hirschfelder (1961). These two potentials will be abbreviated as BRH and KTH respectively.

COMBINATION RULES

The development of such relations which may permit the determination of the unlike molecular interactions from the related like interactions is very useful for it then becomes possible to calculate the different properties of mixtures also. Such relations, usually referred as combination rules, are not known for the BCK potential. We present below the development of such expression. This has been done in brief for the pertinent arguments involved have been stated earlier in many papers. Equation (1) is easily transformed to the following convenient form :

$$\phi(r) = Ae^{-Br} - D/r^6, \qquad \ldots \quad (2)$$

where

$$A = \frac{6\epsilon e^6}{br^{*6}}, \quad B = b/r_m, \quad \text{and} \quad D = \epsilon \frac{(6+b)}{b} r_m^6, \qquad \ldots \quad (3)$$

and r^* is the reduced value of r such that $r^* = r/r_m$. As shown by Zener (1931) the value of B corresponding to the unlike molecules can be written in terms of the like molecules as,

$$B_{12} = (1/2)(B_{11} + B_{22}). \qquad \ldots \quad (4)$$

The theories of despersion forces first given by London (1930) and further approximated by Beattie and Stockmayer (1951) suggest the geometric mean rule for D so that

$$D_{12} = (D_{11} . D_{22})^{\frac{1}{2}}. \qquad \ldots \quad (5)$$

Theory provides no clue for suggesting a combination rule for the parameter A. Some empirical arguments and more the success achieved in connection with the other potentials prompt us to assume a geometric mean rule for A also. Consequently we get

$$A_{12} = (A_{11} \cdot A_{22})^{\frac{1}{2}} \qquad \ldots \quad (6)$$

Substituting the values of different D_{ij} and A_{ij} from *Eq.* (3) in Eqs. (5) and (6) respectively, and then dividing the former by the latter we get the following transcendental equation for evaluating the parameter b_{12},

$$\frac{b_{12}+6}{e^{b_{12}}} = \left[\frac{b_{11}+6}{e^{b_{11}}} \cdot \frac{b_{22}+6}{e^{b_{22}}} \right]^{\frac{1}{2}}. \qquad \ldots \quad (7)$$

Again the substitution of different B_{ij} in Eq. (4) from Eq. (3) leads directly to the following explicit relation for $(r_m)_{12}$ in terms of b_{12} and other constants characteristic of pure interactions. This is

$$(\gamma_m)_{12} = \frac{2b_{12}}{b_{11}/(r_m)_{11}+b_{22}/(r_m)_{22}} \tag{8}$$

Similarly the required relation for ϵ_{12} emerges when one substitutes in Eq. (6) the values of different A_{ij} from Eq. (3), which is

$$\epsilon_{12} = (\epsilon_{11} \cdot \epsilon_{22})^{\frac{1}{2}} \frac{b_{12}}{(b_{11} \cdot b_{22})^{\frac{1}{2}}} \cdot \left[\frac{(r_m)_{11} \cdot (r_m)_{22}}{(r_m)^2_{12}} \right]^{\frac{1}{2}} \cdot \frac{e^{\frac{b_{11}+b_{22}}{2}}}{e^{b_{12}}} \quad \ldots \quad (9)$$

The relations (7), (8) and (9) are to be employed for computing b_{12}, $(r_m)_{12}$ and ϵ_{12} respectively and hence the so called combination rules.

POTENTIAL PARAMETERS

The approach of Carra' and Konowalow (1964) for determining the three parameters b, ϵ/K and r_m of BCK potential is somewhat objectionable. This is because they have employed the crystal energy data and assumed the validity of the pairwise additivity rule. We have therefore evaluated the potential parameters from the temperature dependence of $B(T)$ data alone. The parameter b of the BCK potential is related with the parameter α of the modified exp-(6) potential, Carra' and Konowalow (1964), as

$$b = \alpha - 6. \tag{10}$$

This relation results by equating the values of $\phi(r)$ on the two potentials at the minimum. To start with we have also assumed the relation of Eq. (10) and determined the remaining two parameters ϵ/k and tr by adopting the familiar method of translation. A log-log plot of the reduced virial coefficient B^* (b, T^*), is drawn against T^* the reduced temperature for a particular value of b characteristic of the gas under investigation. A similar log-log plot of experimental $B(T)$ against T is next prepared on a transparent graph paper emplying the same scale as in the previous plot. The latter plot is next moved over the former and an effort is made to best coincide the two by translations parallel to the two axes. The magnitudes of translation along the X and Y axes yield the values for ϵ/k and r_m respectively. The values so obtained are recorded in Table 1. The references to the experimental data employed are given in the last column of this very table.

The parameters for the unlike interactions can now be calculated according to the Eqs. (7), (8) and (9) and the like parameters recorded in Table I The values of these unlike parameters are reported in Table II.

COMPARISON OF THEORETICAL AND EXPERIMENTAL SECOND VIRIAL COEFFICIENT

The second virial coefficient of a pure gas, $B(T)$, as given by Hirschfelder, Curtiss and Bird (1954), is

$$B(T) = 2/3\pi N r_w^3 B^*(b, T^*), \quad \ldots \quad (11)$$

where N is the Avogardo number. Utiling the tabulations of Carra' and Konowalow for B^* (b, T'^*) in conjunction with the parameters given in Table II, $B(T)$ was calculated at all those temperatures where direct measured values are available. We do not report here all these calculations for the sae of brevity. However in Table III column 2 we list for all the gases average absolute deviations, $\overline{\Delta}$. The latter being the difference of the experimental and calculated values of the second virial coefficient.

TABLE I

Potential parameters for like interactions

Gas	Parameters b	ε/K °K	r_m °A	References
He	6.5	4.53	3.084	
Ne	8.5	36.31	3.018	
Ar	8.0	125.9	3.828	
Kr	6.3	152.7	4.295	
Xe	8.0	231.2	4.585	
H_2	8.0	32.61	3.263	
CH_4	8.0	155.6	4.244	

TABLE II

Potential parameters for unlike interactions

Gaspairs	Parameter b_{12}	ε_{12}/K °K	$(r)_{m12}$ A°
He-Ne	7.5	12.97	3.047
He-Ar	7.25	23.14	3.456
Ne-Ar	8.25	71.94	3.363
Ne-Kr	7.41	91.1	3.458
Ar-Kr	7.15	144.9	4.029
He-H_2	7.25	11.82	3.180
Ar-H_2	8.0	64.50	3.523
Ar-CH_4	8.0	140.7	4.013

TABLE III

Comparison of average absolute deviations, $\bar{X}$, in cc/mole for pure gases

Gas	BCK set I	BCK set II	BRH	KTH
He	0.14	—	0.18	1.41
Ne	0.78	1.15	0.91	0.72
Ar	2.56	2.51	3.74	5.71
Kr	11.38	18.39	5.55	7.66
Xe	1.56	3.28	7.89	2.42
H_2	0.31	—	0.42	0.36
CH_4	0.10	—	0.37	1.31

TABLE IV

Comparison of average absolute derivations, $\bar{X}$, in cc/mole for binary gas pairs

Gas pair	BCK	BRH	KTH
He-Ne	0.51	0.59	0.99
He-Ar	1.48	3.14	5.03
Ne-Ar	18.6 , 8.6	24.5 , 14.8	20.1 , 10.4
Ne-Kr	12.6	16.0	7.4
Ar-Kr	19.1	4.75	18.3
He-H_2	0.76	0.68	1.66
Ar-H_2	0.58	0.63	0.69
Ar-CH_4	3.55	1.55	2.08

Set I refers to the values obtained on the basis of the potential parameters determined here, while set II employs those reported by Garra' andKonowalow.

The second virial coefficient of a binary mixture $B_{mix}(T)$, is given by the following expression (1954)

$$B_{mix}(T) = X_1^2 B_{11} + X_2^2 B_{22} + 2X_1 X_2 B_{12}. \quad \ldots (12)$$

Here X_1 and X_2 are the mole fractions of the components 1 and 2 respectively, $B_{11}$and B_{22} are the $B(T)$ values for the components 1 and 2 respectively, and B_{12}

is the virial coefficient of a hypothetical pure gas shose molecules interact according to the potential law for (1, 2) interaction. $B_{mix}(T)$ values were computed for the eight gas pairs at all those temperatures where directly observed values are available. Again for conciseness we do not report all these calculations but instead are given in Table IV column 2 the average of the absolute differences between the observed and calculated values, X. The experimental data used here are due to the authors Fender and Halsey (1962), Thomaes and Steenwinkel (1962), Gibby, Tanner and Masson (1929), Edwards and Rooserveare (1942), and Knobler and Beenakker (1959).

It will be noted from the entries of column 2 Table III that the reproduction of $B(T)$ values is satisfactory for helium, neon, argon, xenon, hydrogen and mthane in as much as deviations are always within the limits of experimental uncertainties. The situation for the case of krypton is very unsatisfactory and the discrepancy is more than can be explained on the basis of experimental uncertainties. We have also calculated the $B(T)$ values for neon, argon, krypton and xenon utilising the potential parameters of Carra' and Konowalow (1964). The $\overline{X}$-values for all these gases are listed in Table III column 3. It is important to note that discrepancies in all cases except argon are now more than in the previous case and particularly for krypton this difference is appreciable.

Similarly we notice from Table IV that for the gas pairs helium-neon, helium-argon, helium-hydrogen, argon-hydrogen and argon-methane the agreement between the experimental and calculated $B(T)$ values is good. On the other hand for neon-argon, neon-krypton and argon-krypton the reproduction of $B(T)$ values is quite poor. According to Saxena and Gambhir (1963) experimental value for neon-argon gas pair is likely to be in error (1963). Thus, in binary gas pairs we find that agreement between theory and experiment is always satisfactory except when krypton constitutes as one of the components. The failure of the BCK potential to explain the data of krypton is not very strange and has been noticed earlier also in connection with other potentials, Bahethi and Saxena (1964).

In order to have an absolute assessment of this potential in relation with the BRH and KTH potentials it is essential to know the values of $\overline{X}$ for these two potentials for systems of Tables III and IV. Employing the most commonly used parameters and suitable tabulations virials were calculated for all these gases and gas pairs and $\overline{X}$ computed. These values are recorded directly in Tables III and IV. A critical study of the two tables reveals that leaving krypton in all cases BCK potential is better than the two other potentials. BHR potential also seems to be somewhat preferable over the KTH potential. The uniqueness of the behaviour of krypton seems to be inherent in all the three potentials. It is important to note that in BHR potential the parameters were determined by considering both the second virial, viscosity and crystal data but α was treated as a completely disposable parameter. In the case of KTH potential the parameters

were determined from $B(T)$ data alone or in combination with crystal data. Thus the comparison between BCK and KTH potentials may be regarded as equivalent in most of the cases. To get a more clear picture about the relative merits of BCK and BRH potentials we undertake certain more investigations in the next section.

DISCUSSION ON INTERMOLECULAR POTENTIALS

As pointed out in the last section BCK potential fails to reproduce the $B(T)$ data for krypton. The deviation between the experiment and theory is pronounced and somewhat alarming only at low temperatures ranging upto 170°K. It is important to note that at still higher temperatures upto 873°K the theory does succeed in reproducing the experimental data within the margin of experimental uncertainties. The situation is relatively superior for the BRH potential and even for the KTH potential to some extent. We therefore reexamine the krypton $B(T)$ data and make an attempt to determine the three parameters independently without assuming the relation of Eq. (10) for b. We include also argon data for a similar analysis though for this gas BCK potential has been found to be superior to both BRH and KTH potentials. Another consideration which weighed with us to include this gas is the availability of its $B(T)$ data over a very extensive temperature range 85-873°K.

The procedure adopted for determining the three parameters of the BCK potential is somewhat similar to that earlier described in section 3 except now the theoretical log-log plotsare drawn for several probable values of b.

While moving the experimental log-log plot over the theoretical plots an attempt is made to fix the parameter b on the criterion of best fit. The values of the potential parameters so obtained for argon and krypton are reported in Table V. The reproduction of the $B(T)$ data on the basis of these parameters improves remarkably as compared to the one obtained on the basis of the parameters of Table I. To give an idea we quote the average absolute deviation of the computed values from the experimental values. These are 1.08 and 3.26 cc/mole for argon and krypton respectively. A further check is possible on the suitability of these parameters by performing calculations on binary systems which involve these gases. We investigated the systems argon-krypton and neon-krypton in this light. However the calculations revealed only inappreciable improvement. This of course should not be regarded as disappointing. As regards the absolute values of the potential parameters are concerned these are reported in Table VI and are appreciably different than those of Table II. The mixture $B(T)$ values for these systems are available only over a limited temperature range and it so happens that the changes produced in the computed $B(T)$ values from the variations in thevalues of the potential parameters cancal each other such that the overall values remain unaffected. We are of the opinion that in general it would be more appropriate to determine the three parameters of the BCK potential by treating all the three

parameters as completely disposable at least in those cases where elaborate experimental data are available.

TABLE V

Potential parameters for argon and krypton

Gas	b	ε/K °K	r_m A°
Ar	8.5	128.8	3.828
Kr	7.0	156.7	4.362

TABLE VI

Potential parameters for gas pairs

Gasfpair	b_{12}	ε_{12}/K °K	(r_m) A°
Ar-Kr	7.75	149.7	4.053
Ne-Kr	7.75	102.4	3.506

TABLE VII

Values of parameters c' and b' as computed from Eqs. (13) and (14)

Gas Parameter	He	Ne	Ar	Kr	Xe	H_4	CH_2
C*	4.0	5.1	5.0	4.5	4.9	5.0	4.9
C′	4.2	5.0	5.0	4.5	4.6	5.3	4.9
b	6.5	8.5	8.0	6.3	8.0	8.0	8.0
b′ (set I)	17.7	7.3	6.6	7.1	7.9	8.4	7.1
b′ (set II)	—	8.7	7.2	4.9	6.9	—	—

*These values are taken from Konowalow, and Hirschfelder, 1961.

In literature it has been often attempted to compare parameters on the basis that the plot of $\phi(r)$ versus r has the same curvature at the minimum for all. Thus a relationship between the parameter C of the KTH potential with that of the

BRH potential was given by Konowalow and Hirschfelder (1961). This leads finally to the result that

$$C' = \left[\frac{3\alpha(\alpha-7)}{(\alpha-6)} \cdot \frac{\epsilon(BRH)}{\epsilon(KTH)} \cdot \frac{\sigma^2}{r_m^2} \right]^{\frac{1}{3}} \quad \ldots (13)$$

Similarly one can relate b of the *BCK* potential with α of the *BHR* potential to get

$$b'+5 = \frac{\alpha(\alpha-7)}{(\alpha-6)} \cdot \frac{\epsilon(BRH)}{\epsilon(BCK)} \cdot \frac{r_m^2(BCK)}{r_m^2(BRH)} . \quad \ldots (14)$$

In Eqs. (13) and (14) C' and b' respectively are the values of c and b when the curvatures at the minimum for the *KTH* and *BCK* potentials are made equal to that for the BRH potential. These values of c' and b' are reported in Table VII. It will be noted from this table that for the KTH potential the agreement between the c' and c values is quite good indicating thereby a lot of similarity between the *KTH* and *BRH* potential. On the other hand the agreement between b' and b values is rather poor. This suggests that the *BCK* potential has somewhat different character in the short range intermolecular forces compared to the BRH potential. This further suggests that relation given by Eq. (10) should be assumed only when an independent accurate determination of b is not possible.

CONCLUSIONS

We wish to make the explicit mention of the following conclusions in view of the studies presented in this paper :

1. The *BCK* three parameter potential seems to be adequate enough to correlate the second virial data of pure gases and binary gas mixtures. At present the limitations of the available theoretical tabulations do not permit a check of this potential against other porperties.

2. This potential completes favourably with the two other widely studied three parameter potentials. It is likely that it may supersede even the BRH potential which has been enjoying the status of being the best potential for correlating the different properties of gases and gas mixtures. Certainly this new *BCK* potential seems superior to the *KTH* potential.

3. In view of the great promise associated with the BCK potential we feel that the scope of work on this potential be increased by including the particular calculations relevant for the other equilibrium and non-equilibrium properties of gases and gas mixtures.

ACKNOWLEDGMENTS

We are thankful to Dr. D. D. Konowalow for his interest and encouragement in the work presented here. This research was supported by the Council of

Scientific and Industrial Research, New Delhi. The award of a research scholarship to one of us (V.P.S.) is also gratefully acknowledged.

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